

Coal: Kinetic Analysis of Thermogravimetric Data-(II)

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INTRODUCTION

It is customary to use a thermogravimetric analyzer (TGA) to determine the kinetic parameters during coal decomposition. Several workers [1-3] have however, shown that a differential thermal analyzer (DTA) which is used to monitor the change in enthalpy [4] during decomposition can also be used to evaluate the experimental activation energy E , the order of reaction and the pre-exponential factor. This work compares results obtained using a DTA to those obtained using a TGA. For the purpose of statistical evaluation of the variance resulting from using the two methods, the effect of additives was also included.

THEORETICAL

The rate of coal devolatilization may be represented as follows [4-6]:

$$\frac{dC}{dt} = A(1-C)^n \exp[-E/RT] \quad (1)$$

where dC/dt is the rate of reaction, C is the fraction reacted ($0 \leq C \leq 1$), A is the pre-exponential factor, n is the order of reaction, E is the activation energy, R is the gas constant and T is the absolute temperature. Equation 1 can be rearranged and modified to incorporate the heating rate, dT/dt :

$$\log_e [(dC/dt)/(1-C)^n] = \log_e [A/(dT/dt)] - (E/RT) \quad (2)$$

A plot of the left hand side of equation (2) vs $(1/T)$ for various assumed values

of n provides a number of curves. The kinetic parameters are obtained when the results fall along a straight line. A number of such curves are shown in Figures 1 and 2. However, the values of n and E shown in Table 1 were machine computed. The assumed values of n were increased from 0 to 2 in fractions of ten. In DTA work C is the ratio of the reaction enthalpy of the sample at given temperature divided by the total sample enthalpy, and is therefore obtained by dividing the area under the peak at this temperature by the total peak area [1] as illustrated in Figure 3.

EXPERIMENTAL

1. Material

A subbituminous coal (-270 and +320 U.S. mesh) was used which was provided by the Institute of Mineral Research at Michigan Technological University. The properties of the coal are given elsewhere [7-8].

The gas atmosphere was oxygen-free nitrogen and was provided by the Matheson Company. The flow rate was fixed at 50ml/min at STP.

The additives were group 1A metal salts, certified grade Li_2CO_3 from Research Organic/Inorganic Chemical Corporations; K_2CO_3 (anhydrous) from Fischer Chemical Company; and Na_2CO_3 (anhydrous) from J.T. Baker Chemical Company.

2. Apparatus

A DuPont Differential Thermal Analyzer with a 1200°C was used. The DTA was operated at a linear heating rate of 20° C/min.

RESULTS AND DISCUSSION

Table 1 summarizes values of E and n for the temperature range (523-923K) obtained using both DTG and TGA, as well as the effect of alkali metal salts. The corresponding values of n and E obtained using DTA and TGA (method 2) show little variance. Both methods are similar in that the order of reaction is determined by trial and error. The better agreement of E values, obtained by DTA and method 1 (TGA) is interesting considering that in the latter procedure, n was assumed equal to unity in equation 1.

To determine the significance of the observed variations in the values of the activation energy resulting from the use of different instruments, methods and metal salts, the variance was analyzed using an Analysis of Variance Table (Table 2). On the basis of the F-ratio test it was possible to conclude that the variance due to the methods and instruments was not statistically significant. However, changing the additive type produced a significant effect.

The good agreement between corresponding values of E and n may have been due to the similarity of a DTA curve and the curve representing the rate of conversion (dC/dt) obtained using a TGA [9]. Another factor may have been that the maximum difference temperature ΔT_{\max} and $(dC/dt)_{\max}$ occurred at nearly the same temperatures. This was found to be the case (Table 3), however, ΔT_{\max} occurred at a slightly higher temperature. The thermocouple in DTA work was touching the sample holder which may have reduced the actual heating rate of the sample. This was not expected to affect the measured peak temperature due to the small radius of the sample [10]. The shape of the sample holder and loose packing in the case of the TGA provided better contact between the flowing gas and the sample, which may have accounted for the occurrence of $(dC/dt)_{\max}$ at a lower temperature.

Two other DTA methods [2,3] for measuring E and n were also considered and found to be less attractive than the method adopted in this work. Both involved

measuring an inflection temperature, T_i , and the temperature at which ΔT_{\max} occurred off a DTA thermogram. It was therefore to be expected that the precision would be low. This was especially true when plots were small or not very smooth. Also, in the method proposed by Kissinger [2] two thermograms were required to evaluate E and therefore, the results would depend on the heating rate combination used [5].

CONCLUSIONS

A DTA thermogram may be used to obtain kinetic data given that the variance between DTA and TGA results was statistically insignificant.

References

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Table 1

Kinetic Parameters: Influence of Method and Alkali Metal Salts

Experimental Conditions	TGA [7]				DTA	
	Method 1		Method 2			
	n	E _{II}	n	E _{II}	n	E _{II}
Coal	1.0	50.9±2.3	0.52±0.04	46.1±1.2	0.6	51.2±2.7
Coal + Li ₂ CO ₃	1.0	35.2±3.1	0.38±0.04	41.7±0.9	0.4	39.6±2.2
Coal + Na ₂ CO ₃	1.0	45.6±2.5	0.44±0.04	43.1±1.1	0.5	46.6±2.6
Coal + K ₂ CO ₃	1.0	49.1±2.3	0.48±0.04	45.0±1.1	0.5	50.4±2.6

E= KJ/mol ; n=order of reaction

Table 2

Analysis of Variance Table (ANOVA)

Source of Variation	Degree of Freedom	Sum of Squares	Mean Square	F-ration	F-ratio (from table)
Additives	3	200.59	66.86	9.35	F _{3,6,0.95} =4.76
Methods	2	17.88	8.94	1.25	F _{2,6,0.95} =5.14
Error	6	42.89	7.15		
Total	11	261.36			

Table 3

Furnace Temperatures at Which ΔT_{\max} and $(dm/dt)_{\max}$ Occurred

Experimental Conditions	TGA [7] $(dm/dt)_{\max}$	DTA ΔT_{\max}
Coal	720K	753K
Coal + Li ₂ CO ₃	698K	728K
Coal + Na ₂ CO ₃	708K	743K
Coal + K ₂ CO ₃	713K	748K

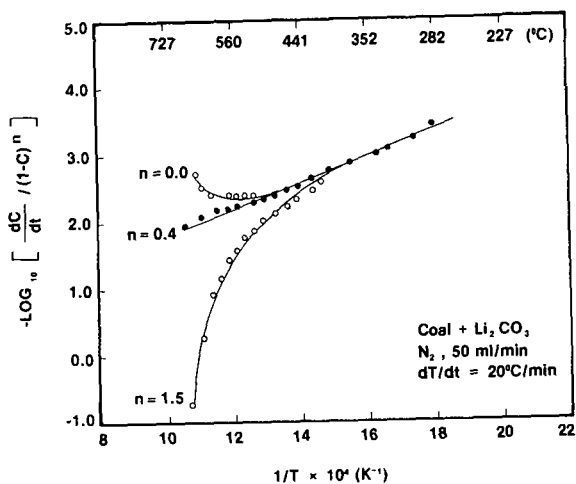


Figure 2: Plots of nth order equation
for coal - Li_2CO_3 mixture

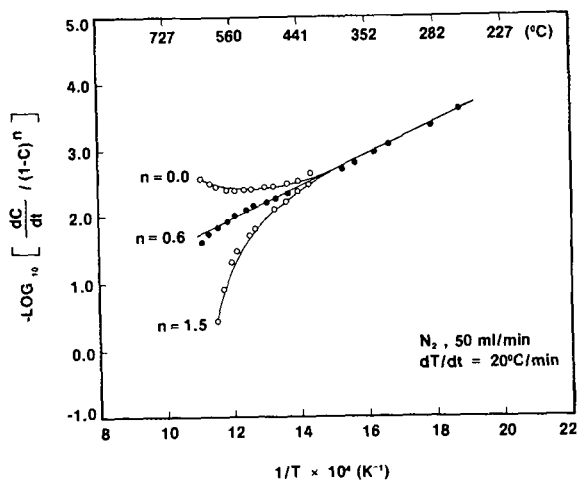


Figure 1: Plots of nth order equation
for coal

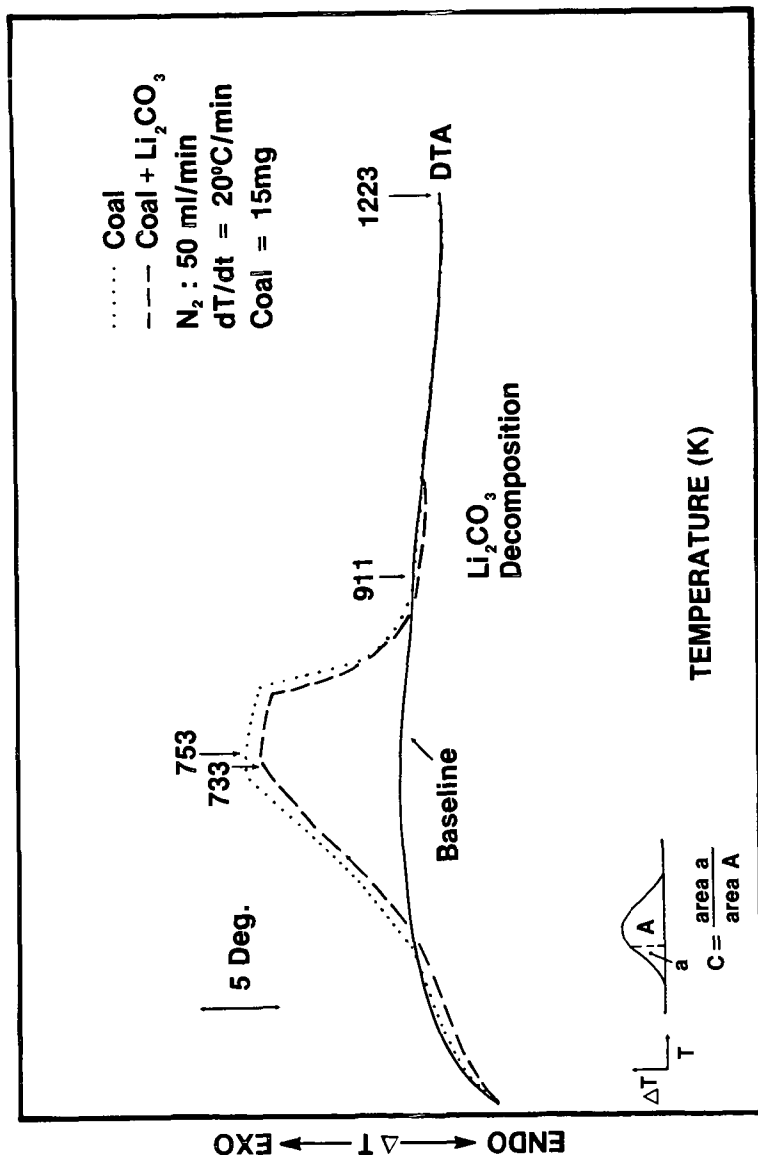


Figure 3: DTA heating curve for coal and Li_2CO_3 - coal mixture in nitrogen (10^5 N/m^2)